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XIV.

ON THE COMPOSITION OF CERTAIN PETROLEUM OILS, AND OF REFINING RESIDUES.

BY CHARLES F. MABERY.

Presented October 8, 1890.

IN an examination of crude Lima oil that I had occasion to make in the early development of the Ohio oil fields in 1885, I observed the peculiar penetrating odor of the sulphur compounds; and while they were present in all fractions during distillation, I noted that they collected principally in the portions with higher boiling points, between 200° and 300° . A systematic examination of the oil was soon undertaken for the purpose of ascertaining the form of the sulphur compounds; but little was accomplished when the work was interrupted by a destructive fire, and it was not resumed until two years later.

In published accounts of the composition of petroleum oils I have found very few allusions to the presence of sulphur, and those that appear are limited to the products of distillation. Hagar* found carbonic disulphide in petroleum ether, but none in burning oil. H. Vohl† reported sulphur in considerable quantities as sulphuric acid in numerous samples of crude (Roh) petroleum. But from the data given and allusions to the products as burning oils, they had undoubtedly been refined with the aid of sulphuric acid. Much difficulty has been experienced in the removal of sulphur from the distillates of Ohio oil, and consequently few if any of the commercial products are entirely free from sulphur, while it is frequently present in considerable quantities.

This paper contains a description of results thus far obtained, of which the following is a summary:—

1. The separation and identification of methyl, ethyl, normal propyl, iso- and normal butyl, pentyl, ethylpentyl, and hexyl sulphides, which are present in crude Ohio petroleum.

* Jahresb. Liebig, 1867, p. 947, Aus Pharmac. Centrale.

† Ibid., 1875, p. 1053; Dingl. Journal, ccxvi. 47.

2. The separation of certain sulphides that do not correspond in boiling points nor in composition with any sulphides hitherto described, which will be further examined.

3. The separation of certain sulphur free oils apparently unsaturated that also require further study.

I am not aware that these alkyl sulphides have hitherto been identified as natural products.

I. THE SULPHUR COMPOUNDS IN OHIO PETROLEUM.

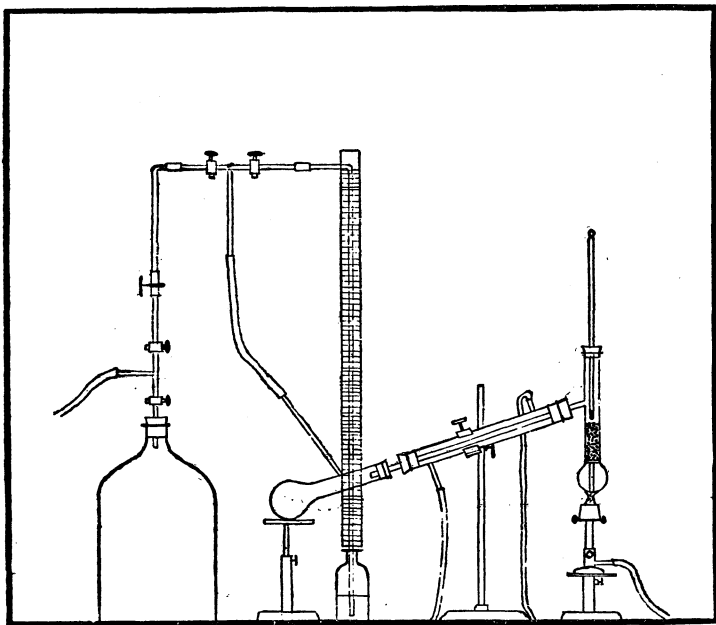
BY CHARLES F. MABERY AND ALBERT W. SMITH.

When the various distillates from Ohio oils are agitated with concentrated sulphuric acid, the sulphur compounds are partially removed in combination with the acid. By neutralizing the acid solution with plumbic carbonate, filtering, and evaporating carefully, lead salts soluble in water are obtained that are easily decomposed by heat with the formation of plumbic sulphide. If the acid solution is neutralized with calcic carbonate or calcic hydrate, unstable calcium salts are formed that are readily decomposed by distillation with steam, which carries over the sulphides without decomposition.

In applying a mode of separation from the crude oil of the sulphur compounds based upon these observations, we procured fifty litres of what is technically known as sludge acid that had recently been used in refining Lima burning oil, and after dilution we neutralized it in the cold with slaked lime and distilled the mixture of solution and solid with steam. We thus obtained 2,270 grams of the sulphur oil that was colorless when freshly distilled, and entirely free from hydric sulphide. Analysis showed that it contained 14.97% of sulphur with a specific gravity at 16°.5 of 0.9245. Analyses of samples of crude Ohio oils from different localities have given on the average about 0.50% of sulphur.

Distillation under atmospheric pressure of the oil distilled with steam produced such serious decomposition that we were forced to conduct all fractional separations with diminished pressure; but since the decomposition was inappreciable at tensions reduced to 150 mm., this involved but little additional labor, except in the inconvenience of maintaining the required tensions with the use of common corks without lutings, which became necessary on account of the solvent action of the oil. The fractional distillations were carried on in the apparatus represented in the accompanying diagram; while it contains no features not hitherto described, it may serve to illustrate how such

an apparatus can readily be arranged to work satisfactorily from material always at hand in the laboratory. Hill's* application of the Hempel device, which consists in supporting glass beads in the neck of the distillation flask on a piece of glass rod with one end



enlarged, is a means of saving much time in a long series of separations. The receiver is simply a second distillation flask. This form of manometer was most convenient, since hydric sulphide was evolved to a certain extent, and, the manometer tube becoming discolored by mercuric sulphide, occasionally it had to be cleaned. In exhausting the apparatus we used an ordinary glass water-pump, and to avoid loss of time in disconnecting the flask, a ten-litre bottle was inserted as a reservoir with stopcocks necessary for continuous action, and a nipper tap with an enlarged thumbscrew was also attached for closely adjusting the pressure.† With this apparatus there is scarcely more

* These Proceedings, xxiv. 342.

† We were unable to use the convenient device of Anschütz for maintaining constant tensions, since the current of air produced considerable decomposition of the oils.

interruption to continuous distillation than at atmospheric pressure. From 1,000 grams of the oil at the end of the sixth distillation, with a tension of 150 mm., the following weights were obtained :—

Temperatures .	−70°	70–80°	80–90°	90–95°	95–100°	100–105°
Grams . . .	12	8.5	16	16	26	20.5
Temperatures	105–110°	110–115°	115–120°	120–125°	125–130°	130–135°
Grams . . .	31	30	83	47.5	59	66
Temperatures	135–140°	140–145°	145–150°	150–155°	155–160°	+160°
Grams . . .	69	56.5	75	36	40.5	230
Total	921.5					

At the end of the twenty-second distillation, with the tension reduced to 100 mm., the products collected to a large extent within well defined limits of temperature and several determinations of sulphur gave the following results :—

Fraction	−76°	80–90°	98–101°	135–145°	148–155°	185–200°
Per cent sulphur .	2.60	7.34	18.23	15.52	16.44	14.21

All fractions containing sulphur gave precipitates with alcoholic and with aqueous mercuric chloride, which were either crystalline, or, with the less volatile products, thick viscous oils. The latter usually became solid on standing, or when crystallized from benzol. As a qualitative test for sulphur, we depended upon the exceedingly delicate nitro-prussid reaction, which was especially serviceable in separating sulphur oils from those containing no sulphur. The platinum compounds R_2SPtCl_4 were readily formed with chlor-platinic acid with evolution of hydrochloric acid. With bromine all fractions united with great energy with the formation of oils heavier than water. These reactions suggested the presence of sulphides, or with sulphur free oils the reaction with bromine indicated unsaturated hydrocarbons.

When distilled at temperatures above 140° atmospheric pressure, the oils became thick and dark in color, and hydric sulphide was freely evolved. Since at lower temperatures the decomposition was slight, the fractional separation of the products collected below 101° (P = 100 mm., see above) was carried further. The products thus collected below 125° united readily with concentrated hydrobromic acid when heated, forming oils heavier than water. The fraction 80–90° was nearly all converted into the heavy addition product, and the fraction 90–100° separated into two products, one heavier

and one lighter than water, the latter in somewhat smaller quantity than the former. The addition product from the fraction 80–90° possessed the characteristic odor of the substituted paraffine hydrocarbons, and upon analysis it gave a percentage of bromine corresponding to monobromheptylen.

0.1850 gr. of the substance gave 0.1116 gr. AgBr.

	Calculated for $C_7H_{15}Br$.	Found.
Br	46.93	46.57

With bromine this product united with a violent reaction, and the resulting oil gave a percentage of bromine required for dibromheptylen.

0.1938 gr. of the substance gave 0.2797 gr. AgBr.

	Calculated for $C_7H_{14}Br_2$.	Found.
Br	62.01	61.42

This fraction therefore consists principally of a heptylen, and it is probably identical with the heptylen obtained by Pelletier and Walthier from the coal oil of Amiano.*

Upon the addition of alcoholic mercuric chloride to fraction 110–125° atmospheric pressure, a finely crystalline precipitate was formed that contained a percentage of mercury required for methyl sulphide.

0.3156 gr. of the mercury compound gave 0.2214 gr. HgS.

	Calculated for $(CH_3)_2SHgCl_2$.	Found.
Hg	60.06	60.47

The fraction 125–135° also gave a crystalline precipitate with alcoholic mercuric chloride, which after crystallization from benzol gave a percentage of mercury corresponding to ethyl sulphide.

0.5056 gr. of the mercury compound gave 0.3122 gr. HgS.

	Required for $(C_2H_5)_2SHgCl_2$.	Found.
Hg	55.40	55.42

Although the boiling points of the oils from which these mercury addition products were separated were considerably higher than those of the sulphides to which the mercury determinations correspond, these oils consisted to a certain extent of hydrocarbons which were subsequently found to contain no sulphur. The higher fractions gave with mercuric chloride oily addition products which became

* Berz. Jahresb., xxi. 470.

crystalline after washing with alcohol, and separation from hot benzol. The addition product from fraction 150–155° gave 53.33% Hg; calculated for $(C_3H_7)_2SHgCl_2$, 51.41% Hg. It was therefore probably a mixture of propyl and butyl sulphides. From fraction 155–160° the addition product with mercuric chloride gave upon analysis 49.44% Hg; required for $(C_7H_9)_2SHgCl_2$, 47.96% Hg. It therefore still contained a lower sulphide. On account of the small quantity that we obtained of these products, we were unable to separate them more completely.

We will next describe in detail the separation of the various sulphides.

Methyl Sulphide.

Further attempts to separate the lower sulphides were made from the crude naphtha distillate. We procured 250 litres of crude naphtha from Findley oil that nearly all distilled below 150°, and agitated it thoroughly in quantities of five litres each, with aqueous mercuric chloride. The heavy flocculent precipitate that separated was subjected to heavy pressure in a screw press, dried, and decomposed by hydric sulphide in presence of alcohol. For the decomposition of considerable quantities of the mercury addition product, vigorous agitation was necessary, and the mercuric sulphide invariably separated in the red modification. After filtration the alcoholic solution of the oil was diluted with water, the oil collected in a separatory funnel, washed, dried, and submitted to fractional distillation. It was nearly colorless, with a specific gravity at 20° of 0.8543. Under atmospheric pressure the decomposition was less marked than in the case of the oil extracted with sulphuric acid. A small quantity of the oil was collected below 50° that gave a percentage of sulphur corresponding to methyl sulphide.

0.1800 gr. of the oil gave by the method of Carius 0.6672 gr. $BaSO_4$.

	Calculated for $(CH_3)_2S$.	Found.
S	51.61	50.89

Between 60° and 80° the quantity of distillate was too small to prove the presence of methylethyl sulphide. Results of analysis were intermediate between the requirements for methyl and ethyl sulphides, but not sufficiently close for methylethyl sulphide. On account of the great amount of labor involved in the separation of these volatile oils, no further attempts were made to identify this sulphide, especially as its presence was regarded as doubtful.

Ethyl Sulphide.

After long continued fractional distillations, we succeeded in obtaining a product distilling between 88° and 92° that gave a percentage of sulphur corresponding to ethyl sulphide.

0.1632 gr. of the oil gave 0.4183 gr. BaSO_4 .

	Calculated for $(\text{C}_2\text{H}_5)_2\text{S}$.	Found.
S	35.55	34.86

Ethylpropyl Sulphide.

At several points between 91° and 130° , the boiling points respectively of ethyl and propyl sulphides, distillates collected in considerable quantities. A fraction that distilled tolerably constant at $110-112^{\circ}$ contained a percentage of sulphur required for ethylpropyl sulphide.

0.2445 gr. of the substance gave 0.5396 gr. BaSO_4 .

	Calculated for $\left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_3\text{H}_7 \end{smallmatrix} \right\} \text{S}$.	Found.
S	30.77	30.31

The platinum salt was formed by the addition of alcoholic chlorplatinic acid, and it gave on analysis the required percentage of platinum.

0.3240 gr. of the substance gave 0.1158 gr. Pt.

	Calculated for $2(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{PtCl}_4$.	Found.
Pt	36.01	35.75

The quantity of this sulphide that we obtained was insufficient for complete examination, and further study of it, as well as of other fractions of low boiling points, must therefore be postponed until we can secure a larger supply of material.

Normal Propyl Sulphide.

All attempts to isolate isopropyl sulphide were unsuccessful; very little of the distillate collected between 115° and 125° , and analysis showed that it could not be the isopropyl compound that boils at 120° . The fraction $115-120^{\circ}$ gave 29.29% S, and the fraction $120-125^{\circ}$, 28.52% S; calculated for $(\text{C}_3\text{H}_7)_2\text{S}$, 27.12% S. Analysis of platinum salts of these fractions gave similar results. Normal propyl sulphide was readily identified in the fraction $127-132^{\circ}$, which collected in larger quantities.

0.0443 gr. of the substance gave 0.0880 gr. BaSO_4 .

Calculated for $(\text{C}_3\text{H}_7)_2\text{S}$.
27.12

Found.
27.44

The presence of propyl sulphide was further shown by analysis of the platinum salt.

- I. 0.1720 gr. of the salt gave 0.0600 gr. Pt.
- II. 0.1309 gr. of the salt gave 0.0457 gr. Pt.
- III. 0.0930 gr. of the salt gave 0.0329 gr. Pt.

	Calculated for $2(\text{C}_3\text{H}_7)_2\text{S} \cdot \text{PtCl}_4$.	I.	Found. II.	III.
Pt	34.26	34.10	34.92	35.15

Analyses II. and III. were made of preparations from fraction 80–90° ($P = 150$ mm.) that were obtained in fractioning the oil from the sulphuric acid extract. This oil contained only very small quantities of propyl sulphide, or of other lower homologues. It consisted mainly of higher sulphides and of sulphur free oils. The presence of heptylen has been described, and nearly all fractions contained sulphur free oils that united readily with bromine, and those of lower boiling points with hydrobromic acid. The sulphides were separated by dissolving the oil in alcohol, and adding a small excess of alcoholic mercuric chloride. An aqueous solution precipitates the sulphides, but it is apt to carry down the sulphur free oil. The precipitates were usually in the form of a thick viscous mass, although with care they could be obtained crystalline. They were washed with alcohol, and decomposed by hydric sulphide in presence of alcohol. The filtered alcoholic solution was diluted with water, and the sulphide that separated was washed free from hydric sulphide, dried, and again submitted to fractional distillation for analysis.

Upon dilution of the alcohol from the precipitation by mercuric chloride, an oil separates that is lighter than water, and with an exceedingly disagreeable odor. These oils unite readily with bromine and with hydrobromic acid, and they contain no sulphur. Whether they are decomposition products resulting from the action of sulphuric acid upon the sulphur oils, or are normal constituents of the crude petroleum, we have not fully determined. But since the sludge acid showed very little indication of decomposition, it seems probable that the sulphur free oils are abstracted by sulphuric acid during the process of refining.

The composition of the fractioned sulphides before and after treatment with mercuric chloride may be shown by the effect on the

percentage of sulphur. The fraction 135–140° (P = 150 mm., B. P. = 185–190°, P normal) gave 15.40% S. After treatment with mercuric chloride as described above, analysis showed 20.37% S.

The higher sulphides were all obtained from fractions of the oil that was extracted from sludge acid. Those of medium boiling points may be separated in smaller quantities from naphtha distillates by mercuric chloride, which has the advantage that the sulphides are uncontaminated by other products. But this method is exceedingly laborious, and the yields are small. We have in mind a modification that works successfully with small quantities of the mercury addition product. It includes recovery of the mercury by conversion of the sulphide into the sulphoxide.

Ethylpentyl Sulphide.

After the twenty-second distillation (page 221), a sulphide was obtained from fraction 95–100° (P = 100 mm.) through the mercury compound that distilled without decomposition at 156–160°. It gave, upon analysis, a percentage of sulphur required for ethylpentyl sulphide (B. P. 158–159°).

I. 0.2629 gr. of the oil gave 0.4516 gr. BaSO₄.

II. 0.1169 gr. of the oil gave 0.2056 gr. BaSO₄.

S	Calculated for $\left\{ \begin{array}{l} \text{C}_8\text{H}_{18} \\ \text{C}_8\text{H}_{11} \end{array} \right\} \text{S.}$	Found.	
		I.	II.
	24.24	23.59	24.15

Isobutyl Sulphide.

The mercury addition product from fraction 110–115° (P = 100 mm.) was decomposed with hydric sulphide and the alcoholic solution diluted with water. After drying over calcic chloride, the oil thus obtained distilled at 170–176°, which corresponded to the boiling point of isobutyl sulphide (172°) and its composition was further shown by a determination of sulphur.

0.1750 gr. of the oil gave 0.2760 gr. BaSO₄.

S	Calculated for (C ₄ H ₉) ₂ S.	Found.
	21.92	21.66

Normal Butyl Sulphide.

The fraction 117–125° (P = 100 mm.) gave an addition product with mercuric chloride from which an oil was obtained that distilled at 180–185° (B. P. of normal butyl sulphide = 182°), and the percentage of sulphur indicated butyl sulphide.

- I. 0.1633 gr. of the oil gave 0.2657 gr. BaSO_4 .
 II. 0.2929 gr. of the oil gave 0.3236 gr. BaSO_4 .

	Calculated for $(\text{C}_4\text{H}_9)_2\text{S}$.	I.	Found.	II.
S	21.92	22.35		21.07

Butylpentyl Sulphide.

An inspection of the weights collected at different temperatures given on page 220 will show a tendency of the distillates to collect at certain temperatures, and this is especially evident in the fraction 135° – 140° . As the distillation proceeded, the fractions at these points increased in quantity, and, so far as examined, each of them corresponded to a definite sulphide. From the fraction 135° – 140° an oil was obtained by decomposition of the addition product with mercuric chloride that distilled at 185° – 190° (Bar. = 740 mm.) and the percentage of sulphur corresponded to butylpentyl sulphide.

- I. 0.2509 gr. of the oil gave 0.3721 gr. BaSO_4 .
 II. 0.2676 gr. of the oil gave 0.3925 gr. BaSO_4 .

	Calculated for $\left\{ \begin{smallmatrix} \text{C}_4\text{H}_9 \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right\}_2\text{S}$.	I.	Found.	II.
S	20.00	20.37		20.14

It is hardly probable this product was a mixture of butyl and pentyl sulphides, since it was obtained at different times after prolonged distillation. It will be further examined.

Pentyl Sulphide.

This sulphide was separated from the fraction 150 – 155° (P = 100 mm.) by conversion into the mercury compound and decomposition with hydric sulphide. Different preparations from independent fractions distilled with very little decomposition at 205 – 210° (Bar. = 745.5 mm.), which is somewhat lower than the boiling point assigned to pentyl sulphide (216°). But from the results of analysis there can be no doubt as to the composition of this sulphide.

- I. 0.1987 gr. of the oil gave 0.2717 gr. BaSO_4 .
 II. 0.2723 gr. of the oil gave 0.3716 gr. BaSO_4 .
 III. 0.2844 gr. of the oil gave 0.3902 gr. BaSO_4 .

	Calculated for $(\text{C}_5\text{H}_{11})_2\text{S}$.	I.	Found.	III.
S	18.39	18.75	18.74	18.85

It is quite probable that the low boiling point was due to the presence of a very small quantity of a lower sulphide, since the

sulphur determinations are somewhat higher than the percentage required for pentyl sulphide.

Hexyl Sulphide.

From the fraction 160–170° (P = 100 mm.) by precipitation with mercuric chloride and decomposition with hydric sulphide a light yellow oil was obtained that distilled with some decomposition at 225–235°, and it gave a percentage of sulphur required for hexyl sulphide.

0.3110 gr. of the oil gave 0.3531 gr. BaSO₄.

	Calculated for (C ₆ H ₁₃) ₂ S.	Found.
S	15.84	15.59

At least one third of the original oil distilled above the boiling point of hexyl sulphide, but with considerable decomposition even under diminished pressure. It consisted to a very large extent of sulphides, but we have not attempted to separate them for identification.

In order to satisfy any doubt as to whether these sulphides are contained in the crude petroleum, we distilled several litres under diminished pressure to avoid decomposition, and extracted portions of various distillates with sulphuric acid, and other portions with aqueous mercuric chloride. The oils, separated from the acid solution and from the mercuric chloride addition product, resembled in all respects the products previously described. From the distillate corresponding to 150–300° atmospheric pressure, or to the best grades of burning oil, by agitation with aqueous mercuric chloride, the characteristic heavy precipitate was formed, and the oil obtained from it contained 19.72% sulphur and gave all the reactions for sulphides. In separating sulphides from oils extracted with sulphuric acid, we have frequently obtained small quantities of a product with a penetrating odor resembling that of turpentine; and at other times, oils containing no sulphur with an odor characteristic of certain ethereal oils, such as peppermint or pennyroyal. But we have not yet obtained these oils in quantity sufficient for examination.

The study of Ohio oils will be continued, and the investigation will include an examination of oils from other localities for sulphur compounds, and also the composition of other acid residues and by-products obtained in refining petroleum oils.

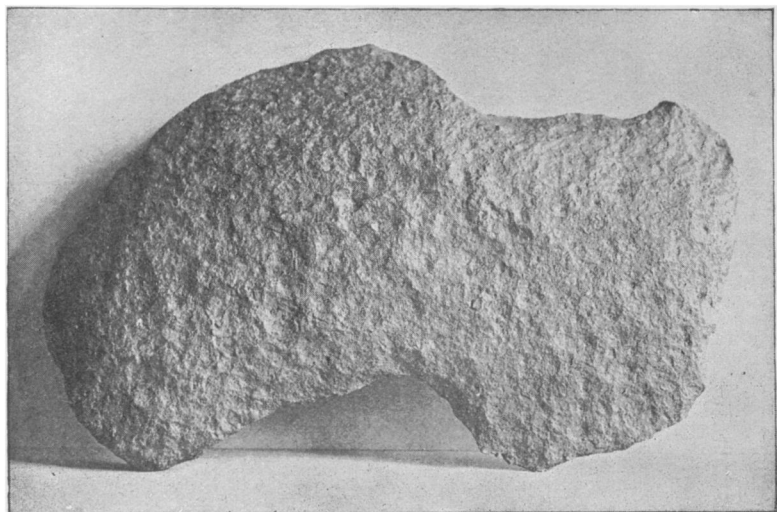


FIG. 1.

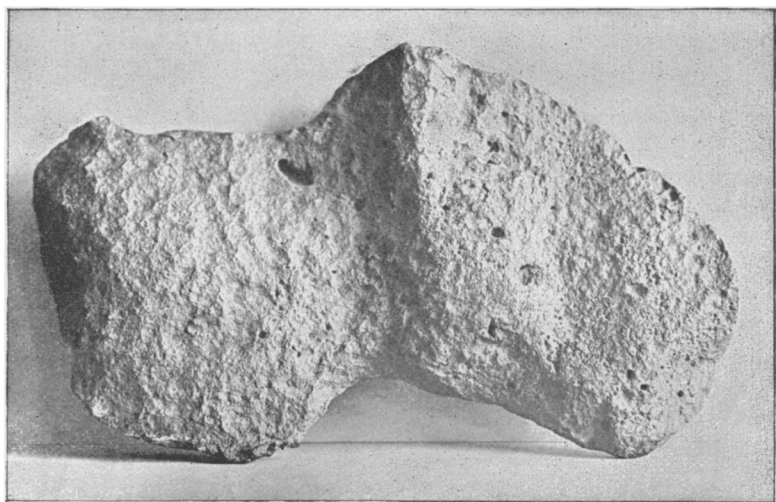


FIG. 2.